Thin Films Division
Room 316 - Session TF2+AP+SE+SS-WeM
ALD and CVD: Surface Reactions, Mechanisms and Kinetics

Moderator: Jessica Kachian, Intel Corporation

8:00am **TF2+AP+SE+SS-WeM-1 Nucleation Enhancement of Ruthenium Atomic Layer Deposition Using Organometallic Molecules***, **Amnon Rothman**, D. Tsousis, S. Bent,* Stanford University

Atomic layer deposition (ALD) is an attractive surface-sensitive thin-film deposition technique used in advanced technologies such as microelectronics, catalysis, and energy applications. The self-limiting surface reactions during the ALD process promote the layer-by-layer growth mechanism, thus providing significant control over the film thickness and conformality. However, due to an island growth mechanism and nanoparticle formation, metal ALD on oxide surfaces can lead to poor-qualify films and display long nucleation delays. One of the main reasons for the nucleation delays can be attributed to the differences in the surface energy between metals and oxide surfaces. In this work, we study the nucleation enhancement of ALD ruthenium layers on Si substrates by using a single monolayer of trimethylaluminum (TMA) or diethylzinc (DEZ) preadsorbed on the substrate prior to deposition. The nucleation enhancement is demonstrated for ruthenium ALD using two different ALD precursors, cyclopentadienylethyl(dicarbonyl)ruthenium(II) (RuCpEt(CO)2) and bis(cyclopentadienyl)ruthenium(II) (RuCp2), with O2 as a counter reactant. The ruthenium ALD nucleation and growth mechanism were studied using scanning electron microscopy (SEM), ellipsometry and X-ray photoelectron spectroscopy (XPS), both on the treated and untreated substrates. The results show that pretreatments using organometallic molecules reduce the nucleation delay of the ruthenium layer. The surface pretreatment strongly influences the ruthenium nucleation, yielding up to a 1.5-fold and a 2.1-fold increase in the surface coverage of the metal while using RuCpEt(CO)2 and RuCp2, respectively. Interestingly, pulsing TMA or DEZ, with or without exposure to H2O, is equally effective. We hypothesize that the high coverage in the pretreated samples is attributed to an increase in the substrate's surface energy, enhancing the surface diffusion of nanoparticles and adatoms during growth. We confirm that exposure of organometallic molecules during ruthenium ALD using the precursors above introduces a potential pathway toward achieving high-quality ruthenium thin films.

8:20am **TF2+AP+SE+SS-WeM-2 Ald of Chalcogenide and III-V Materials for Memory Applications***, **Laura Nyns**, A. Delabie, W. Devulder,* IMEC, Belgium*; J. Girard,* Air Liquide, France*; B. McKeown, V. Pallem,* Air Liquide*; T. Peissker, J. Sinha,* IMEC, Belgium*; N. Stafford,* Air Liquide*; J. Swerts,* IMEC, Belgium **INVITED**

To enable fast and powerful storage solutions for next generation mobile applications and other innovative technologies, the memory landscape focuses on various concepts. These concepts include DRAM for high-speed access, NAND flash memory for storage of large amounts of data, and the emerging Storage Class Memories (SCM) for massive data access in short time. Each of these technologies require their own set of materials with specific characteristics. Additionally, material deposition can be challenging because of the high aspect ratios which are typical for these advanced 3D architectures. Atomic Layer Deposition (ALD) has been shown to be a promising technique in that respect, as conformal deposition of a wide range of materials in complex topographies was established over the past decades. In this talk, we will address the ALD of germanium chalcogenides, a class of materials which is being explored as phase change memory and selector elements for SCM applications. GaAs will also be discussed, due to the need for high mobility channel materials to replace poly-Si in NAND flash technologies. We used the dechlorosilylation chemistry for the ALD of chalcogenide and III-V materials, where (nonmetal) alkylsilyl compounds react with metal chlorides to enable the growth of amorphous layers at low deposition temperatures [1]. An ALD GaAs process could be established, resulting in smooth and stoichiometric films that are amorphous as deposited. Crystallization into the preferred cubic phase was obtained at 350-400˚C, despite the presence of a Ga-rich surface oxide due to air exposure. Irrespective of the excellent step coverage in high aspect ratio structures, we found that these films are prone to delamination. We encountered a comparable challenge with ALD GeSe and $Ge_2Sb_2Te_5$ (GST) using this chemistry, and could demonstrate the benefit of proper surface treatments prior to film deposition to engineer the interface structure and improve layer adhesion. For GeSe, the extension of the existing ALD process [2] to ternary and even quaternary compounds is needed to boost the memory cell performance. We will therefore report on the development of an ALD process targeting GeAsSe deposition. Finally, we explored area-selective deposition (ASD) of chalcogenide materials, as this could greatly simplify the fabrication of complex 3D SCM devices. Our results indicate an impressive selectivity of 96% for GST films of ~22nm on TiN compared to SiO_2, by using the dechlorosilylation chemistry in combination with a dimethylamino-trimethylsilane (DMA-TMS) surface treatment.

[1] Pore et al, ***J. Am. Chem. Soc.***, 2009, **131**, 3478-3480

[2] Haider et al, ***Mater. Adv.***, 2021,**2**, 1635-1643

9:00am **TF2+AP+SE+SS-WeM-4 Plasma-enhanced Spatial ALD of SiO_2 investigated by gas-phase Infrared and Optical Emission Spectroscopy***, M. Mione, V. Vandalon,* Eindhoven University of Technology, Netherlands*; A. Mameli,* TNO-Holst Centre & Eindhoven University of Technology, The Netherlands*; F. Roozeboom,* TNO-Holst Centre & Eindhoven University of Technology, Netherlands*; **Erwin Kessels**,* Eindhoven University of Technology, Netherlands

A spatial atomic layer deposition (ALD) process for SiO_2 using bisdiethylaminosilane (BDEAS, $SiH_2[N(C_2H_5)_2]_2$) and an atmospheric O_2 plasma is reported as well as an investigation of its underlying reaction mechanisms [1]. Within the substrate temperature range of 100-250 ºC, the process demonstrates self-limiting growth with a growth-per-cycle between 0.12 and 0.14 nm and SiO_{-2} films exhibiting material properties *on par* with those reported for low-pressure plasma-enhanced ALD (PEALD) [2].

Gas-phase infrared spectroscopy on the reactant exhaust gases and optical emission spectroscopy on the plasma region are used to identify the species that are generated in the ALD process. Based on the identified species and a calibration procedure, we propose a reaction mechanism where BDEAS molecules adsorb on –OH surface sites through the exchange of one of the amine-ligands upon desorption of diethylamine (DEA, $HN(C_2H_5)_2$). The remaining amine ligand is removed through combustion reactions activated by the O_2 plasma species leading to the release of H_2O, CO_2, CO in addition to products such as N_2O, NO_2, and CH-containing species. These volatile species can undergo further gas-phase reactions in the plasma as indicated by the observation of OH*, CN* and NH* excited fragments in emission. Furthermore, the infrared analysis of the precursor exhaust gas indicated the release of CO_2 during precursor adsorption. Moreover, this analysis has allowed the quantification of the precursor depletion yielding values between 10 % and 50 % depending on the processing parameters. On the basis of these results, the overall surface chemistry of the spatial ALD process of SiO_2 will be discussed.

[1] M. Mione, V. Vandalon, A. Mameli, W.M.M. Kessels, and F. Roozeboom, J. Phys. Chem. C 125, 24945 (2021)

[2] G. Dingemans, C.A.A. van Helvoirt, D. Pierreux, W. Keuning, W.M.M. Kessels, J. Electrochem. Soc. 159, H277 (2012)

9:20am **TF2+AP+SE+SS-WeM-5 Role of Al in Enhancing Growth Rate and Crystallinity in Chemical Vapor Deposition of $Hf_{1-x}Al_xB_2$ Coatings Below 300 °C***, **Kinsey Canova**[1], S. Shrivastav, C. Caroff, L. Souqui, G. Girolami, J. Krogstad, J. Abelson,* University of Illinois at Urbana-Champaign

Transition metal diborides are desirable as hard, low-friction, and wear-resistant coatings for applications in extreme environments. To survive high temperatures, the coatings must have a very low rate of microstructural evolution and must resist oxidation, in particular the loss of boron via evaporation of boron oxide. We previously showed that amorphous HfB_2 films can be deposited by chemical vapor deposition (CVD) using a borohydride precursor, $Hf(BH_4)_4$. However, at T > 600 °C, those coatings crystallize and densify, which leads to cracking, and they oxidize readily. Here, we co-flow an aluminum precursor, trimethylamine alane (TMAA), to deposit ternary $Hf_{1-x}Al_xB_2$ alloy films by CVD at temperatures ≤ 300 °C. This affords excellent film deposition and properties: (i) Al incorporation substantially increases the reaction rate of the HfB_2 precursor, yet the growth still gives good conformal coverage over all surfaces in deep features. (ii) The as-deposited films are nanocrystalline, and the lattice parameters are consistent with a random alloy on the metal sublattice, as opposed to a mixture of HfB_2 and AlB_2 grains. (iii) No elemental Al is detected, so there is not a mechanically soft, low-melting phase. (iv) Annealing films to 700 °C in air creates an Al_2O_3 surface layer that protects the underlying film, and negligible grain growth is observed.

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[1] **TFD James Harper Award Finalist**

To determine a cause of the enhanced growth rate, we performed a matrix of growth experiments vs. precursor pressures and temperature; the Al incorporation rate, which is proportional to TMAA flux, has the strongest effect on rates. We hypothesize that Al consumes the excess boron from the HfB_2 precursor – which contains four boron atoms for every Hf atom – and forms AlB_2. This overcomes the probable rate limiting step of HfB_2 deposition, i.e., the associative desorption of excess boron from the growth surface as B_2H_6, and it is consistent with the improved film crystallinity. Finally, this study provides a guide to the parameters controlling growth rate and composition.

9:40am **TF2+AP+SE+SS-WeM-6 Pushing the Limits of ALD Infilling to Produce Macroscopic Nanocomposites***, **Benjamin Greenberg**, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) infilling is a reliable and popular technique for producing nanocomposite thin films. Typically, ALD precursor dose times on the order of 1 s are sufficient for infiltrating and conformally coating the pores of nanoparticle (NP) networks with thickness on the order of 1 µm or less. In principle, the application space for this nanocomposite production method could be expanded significantly by increasing the NP network thickness to 1 mm or greater. In this work, we investigate the possibility of achieving this scale-up through increasing the ALD precursor dose time by three orders of magnitude. We hydraulically press aluminum oxide nanopowder with particle size on the order of 100 nm to form nanoporous compacts with ~2 mm thickness and ~50% solid volume fraction, and we coat the pores with either Al_2O_3 or ZnO by static-dose ALD, holding precursor vapor in the ALD chamber for >1,000 s per half-cycle. For both coatings, we analyze the ALD chamber pressure traces to understand precursor diffusion and reaction kinetics, and we compare our results to predictions based on a Knudsen diffusion model. For the ZnO coating, we use electrical conductivity measurements, X-ray crystallography, scanning electron microscopy, and energy-dispersive X-ray spectroscopy to evaluate coating composition and uniformity within the nanocomposite, and we compare the ZnO-infilled-Al_2O_3 nanocomposite to a compact of core/shell Al_2O_3/ZnO NPs produced by particle ALD (pALD) in a rotary reactor. Preliminary data suggest that uniform infilling of a macroscopic NP network is possible provided that it can be carried out at a temperature sufficiently low to prevent precursor decomposition.

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